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THE ANALYSIS OF FLUORSPAR

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ABSTRACT

In connection with the standardization of the Bureau of Standards standard sample of fluorspar No. 79, old methods of analysis were tested and modified, and new methods were developed. This paper sets forth the procedures that have been found desirable for the determination of carbonates, silica, calcium fluoride, sulphur, barium, lead, and zinc.

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I. GENERAL CONSIDERATIONS

The determinations that are usually made in fluorspar are those of calcium fluoride, silica, and sulphur. To these may be added calcium carbonate or carbon dioxide, lead sulphide, zinc sulphide, the oxides of iron and aluminum, and barium sulphate, which are occasionally determined, and alkalies, magnesia, titania, zirconia, phosphorus pentoxide and other minor constituents, which are sometimes present and would have to be determined in a complete analysis.

1. CALCIUM CARBONATE

The correct determination of calcium that is present as carbonate in fluorspar is difficult, because it is impossible to dissolve the carbonate without at the same time dissolving some calcium fluoride.

The amount of the latter which dissolves varies with conditions, such as the amount of calcium introduced into solution through solution of the carbonate, or of fluorine through the solution of other soluble fluorides.

If fluorspar is digested with a 10 to 20 per cent solution of acetic acid, practically all of the calcium and magnesium carbonates are dissolved, together with more or less calcium fluoride, iron, aluminum, lead, and possibly zinc. Most of the methods now in use call for such a treatment, followed by more or less elaborate separations and the precipitation of the calcium as oxalate. The latter is then ignited to oxide or titrated with permanganate. Even if these methods should yield consistent results, they entirely ignore other carbonates, such as those of lead, magnesium, iron, and the like, which, if present, must also be regarded as impurities in fluorspar. It would seem more satisfactory, therefore, to determine carbon dioxide directly by treating with acid and catching the gas in a weighed absorbent and to report the carbon dioxide so found as "Total carbonates as CaCO_3 ." Such a determination is not only much more rapid than present procedures but gives more significant and consistent results as well.

If organic matter is known to be absent, it is satisfactory for all ordinary purposes to determine carbon dioxide by heating the sample in the furnace used for determining carbon in steel, if the usual provisions for removing compounds of sulphur are made.¹ This procedure is described in the Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Fluxes, Cinders, and Refractories.

2. SILICA

Most of the methods used for determining silica in fluorspar are modifications of that described by Bidtel.² In such methods the calcium carbonate is removed by extracting with acetic acid. Sulphides are oxidized by roasting with mercuric oxide or by digesting with a solution containing potassium bromide and bromine. The sulphates so formed are usually removed by digesting with ammonium acetate, ammonium citrate, or other solvents and then filtering. Finally the residue is ignited and weighed, and silica is determined by treating with hydrofluoric acid, evaporating to dryness, igniting, and again weighing.

In the absence of appreciable quantities of lead and zinc, fairly accurate results for silica can be obtained by leaching the fluorspar with dilute acetic acid, igniting, weighing, treating with hydrofluoric acid, and again igniting and weighing. Lead or zinc sulphides cause serious errors in such a method, for on ignition these are gradually

¹ W. F. Muehlberg, of the Newburgh Steel Works, Cleveland, Ohio, obtained satisfactory results by applying this method to the analysis of the Bureau of Standards standard sample of fluorspar No. 79.

² J. Ind. Eng. Chem., 4, p. 201; 1912; 6, p. 265; 1914.

oxidized to sulphates. According to Hofman and Wanjukow,³ lead sulphate begins to decompose at about 637° C., while zinc sulphate begins to decompose at about 702° C. The uncertainty as to the oxidation or partial decomposition of these substances necessitates as complete oxidation or removal of them as possible.

Treatment with glacial acetic acid containing 20 per cent of liquid bromine was found to be more efficacious than the potassium bromide-bromine treatment in oxidizing zinc sulphide, but less satisfactory in oxidizing lead sulphide. Both constituents were satisfactorily oxidized by first treating with a solution of bromine in glacial acetic acid and then with a solution of potassium bromide and bromine. Treatment with mercuric oxide was not tried, because mercury vapors are objectionable. In any case the sulphates that are formed can be satisfactorily removed by treatment with ammonium acetate.

Lead and zinc sulphides not removed by the preliminary treatments are oxidized to sulphates during the ignition of the siliceous residue. This should therefore be ignited at temperatures just below 650° C., preferably in a muffle furnace, and the final ignition should not be unduly prolonged.

In spite of the fact that the method to be described and similar methods give fairly consistent results, it is not to be supposed that such results of necessity represent the actual silica content. Some silicates may remain unattacked by the hydrofluoric acid treatment, and changes occurring between the first and second ignitions may cause errors, either positive or negative.

3. CALCIUM FLUORIDE

A direct determination of fluorine is rarely, if ever, attempted in analyses involving the sale of fluorspar. The usual custom is to report the percentage of calcium fluoride as calculated from a determination of the calcium that remains after a preliminary treatment which is intended to remove calcium that is not present as the fluoride. Bidtel's method⁴ or some modification of it is widely used for the determination. In such methods calcium carbonate is first extracted with dilute acetic acid and the silica next volatilized by means of hydrofluoric acid. These treatments leave lead and zinc, which must also be removed. This is accomplished by oxidizing the sulphides to sulphates and then extracting with a solution of ammonium citrate or ammonium acetate containing ammonium citrate.⁵ After the lead and zinc are extracted, together with more or less iron and other constituents, the residue is ignited and converted to sulphate by treatment with sulphuric acid. The sulphate is then weighed and

³ Trans. Am. Inst. Mining Eng., 43, p. 523; 1912; Chem. and Met. Eng., 10, p. 172; 1912.

⁴ See footnote 2.

⁵ Some chemists remove the lead, zinc, iron, and the like by precipitating with ammonium sulphide.

the percentage of calcium fluoride calculated on the assumption that only calcium sulphate is present, or else it is dissolved, the calcium precipitated as the oxalate, and ignited to the oxide or titrated with permanganate. In either case the CaO so found is calculated to calcium fluoride. In some methods the residue left after the extraction of lead, zinc, iron, and the like with ammonium citrate-ammonium acetate is dried, ignited, and weighed as CaF_2 .

In the umpire method to be described calcium carbonate is removed by digesting the sample on the steam bath with a 10 per cent solution of acetic acid and filtering. Sulphides are then decomposed and removed by usual procedures before determining the calcium that is present as the fluoride. In the routine method calcium carbonate and the sulphides are removed at the same time by treating the sample in turn with a solution of bromine in acetic acid, then with a solution of potassium bromide and bromine, and finally with a solution of ammonium acetate.

In any method for the determination of calcium fluoride the following facts should be considered:

(a) Practically all of the calcium carbonate and calcium sulphate in fluorspar can be removed by digesting with 10 to 20 per cent acetic acid and filtering. Glacial, or 50 per cent, acetic acid is not so effective as the more dilute acid. Ignited calcium sulphate is but slowly attacked by dilute acetic acid. Both hydrated and anhydrous calcium sulphate readily dissolve in dilute acetic acid containing a small quantity of ammonium acetate.

(b) Tests show that from 2 to 2.5 mg of calcium fluoride is dissolved when pure calcium fluoride is treated with dilute acetic acid as will be described in the "umpire method." However, if as much as 5 per cent of calcium carbonate is present, the amount of calcium fluoride dissolved in the same treatment is only about 1 mg, the decrease in solubility probably being caused by the common ion effect of the calcium. When pure calcium fluoride is treated as prescribed in the "routine method" from 6 to 7 mg is dissolved. In the presence of calcium carbonate the solubility falls to about 5 mg. As calcium carbonate is present in all commercial fluorspar, a correction of 1 mg is recommended in the umpire method and 5 mg in the routine method.

(c) Any method that is based on extraction with dilute acetic acid will be in error if insoluble compounds of calcium, other than calcium fluoride, are present. For example, if calcium silicate were present, it would remain with the calcium fluoride and would be counted as the latter. Fortunately, there is apparently little to be feared from this source.

(d) The oxidation of sulphides by roasting is not to be recommended, because there is some loss of fluorine, probably the result of the dis-

placement of fluorine by the sulphur dioxide or trioxide that is formed. If the roasted sample is subsequently treated with dilute acetic acid, calcium equivalent to the quantity of fluorine lost will be dissolved, and the results for calcium fluoride will be low. In the routine method sulphides are converted to sulphuric acid, and this exerts a solvent action on the calcium fluoride. Ordinarily this is not serious, but there is a tendency toward low results by the routine method if sulphur is high.

(e) Any lead or zinc that escapes extraction in the treatment with the solution of bromine in acetic acid, the solution of potassium bromide and bromine, and the solution of ammonium acetate as described in the "routine method" causes a positive error in the result for calcium fluoride. The error is small, as a rule, for most of the lead and zinc is extracted and what remains is but partially precipitated when the calcium is precipitated as oxalate.

(f) Calcium fluoride can be decomposed by fuming with either sulphuric or perchloric acid. Perchloric acid is advantageous because the products are soluble, and the perchlorates do not "creep" over the rim of the crucible as badly as do the sulphates. All or nearly all of 1 g of calcium fluoride can be converted to the perchlorate by evaporating to dryness twice with 3 to 5 ml portions of perchloric acid in a platinum crucible. A third evaporation with perchloric acid after transferring the solution from the crucible to a beaker is advisable, because any fluorine still left in the solution will cause low results, especially in the routine method. The perchloric acid may be evaporated rather rapidly, but the residue in the crucible should not be heated too strongly when it is just approaching dryness, because of possible mechanical loss. Perchloric acid is not hazardous unless in contact with strong reducing material at temperatures above 100° C. If organic matter is present, heat with perchloric acid at 100° C., add nitric acid dropwise until reaction ceases, and then heat until the perchloric acid volatilizes.

4. SULPHUR

Sulphur in fluorspar is usually determined by fusing the sample with an oxidizing flux, extracting the melt with water, and finally precipitating and weighing as barium sulphate. Melts obtained with potassium carbonate and potassium nitrate dissolve more rapidly than those obtained with sodium carbonate and sodium nitrate and lead to equally accurate results.

Unless great care is exercised in fusing fluorspar, the very fluid melt will overflow or "creep" over the top and adhere to the outside surface of the crucible. There is little danger of loss, but if a gas flame is used this alkaline film on the outside of the crucible or cover may absorb a considerable quantity of sulphur. Positive errors from this source were found to be as high as 0.04 per cent of sulphur.

The use of an electric furnace in making the fusion is to be recommended, because with proper care there is little chance of contaminating the melt with sulphur from outside sources.

Alcohol or petroleum ether flames may be used as a source of heat, but alcohol flames are somewhat difficult to control, and not all petroleum ether is free from sulphur.

Fluorine accompanies sulphur in the water extract of the melt, and most of it must be removed before barium sulphate is precipitated, lest barium fluoride also be thrown down. Most of the fluorine can be removed by evaporating the water extract twice with an excess of hydrochloric acid, and interference by that which remains in solution can be avoided by using only a slight excess of barium chloride in the precipitation of the sulphate.

II. METHODS OF ANALYSIS

1. FINENESS OF THE SAMPLE

The sample should be ground to pass a No. 80 sieve. Coarser material has a tendency to decrepitate on ignition.

2. DRYING

Fluorspar offers little difficulty in drying or weighing the sample. A sample dried for one hour at 105 to 110° C. is satisfactory.

3. CARBONATES

Determine CO_2 by evolving it with dilute HCl (1:1) ⁶ and absorbing it in ascarite. Less attack on the flask results if H_3BO_3 is also used. If desired, the CO_2 may be absorbed in $\text{Ba}(\text{OH})_2$ and determined by titration. Report as "total carbonates as CaCO_3 ."

The apparatus used by the authors consists of a flask fitted with a small reflux condenser which is followed by bulbs or tubes containing (1) H_2SO_4 , (2) pumice impregnated with anhydrous CuSO_4 , ⁷ (3) "dehydrite" ($\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$), (4) a weighed tube containing ascarite and "dehydrite," and (5) a protecting tube containing "dehydrite." All connections are made by simple mercury seals. P_2O_5 may be used instead of "dehydrite." Dilute HCl (1:1) containing 1 g of H_3BO_3 per 100 ml was used in the evolution of the CO_2 .

A determination of CO_2 by heating the sample in a combustion tube would include organic carbon and possibly a little SiF_4 .

⁶ Prepared by mixing 50 ml of the concentrated acid with 50 ml of water. This system of designating dilute acid is used throughout the paper. For example, dilute HCl (5 : 95) denotes a solution containing 5 ml of the concentrated acid and 95 ml of water. If no dilution is specified, the concentrated reagent is intended.

⁷ Prepared by saturating pumice with a solution of CuSO_4 , drying and heating at 150 to 160° C. for four to five hours.

4. SILICA

Transfer a 1.000 g sample to a 50 ml beaker, add 3 ml of acetic acid-bromine mixture,⁸ cover the beaker, and digest on the steam bath for 10 minutes. Next add 10 ml of water and 10 ml of potassium bromide-bromine mixture⁹ and digest for 40 minutes. Finally add 5 ml of a 50 per cent solution of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ and digest for 10 minutes. Add a little paper pulp and filter on a paper of close texture. Wash with 30 to 40 ml of hot water, ignite in platinum at approximately 650°C ., cool in a desiccator, and weigh. Treat with about 3 ml of HF, break up the lumps or cakes with a platinum rod, and evaporate to dryness. Repeat the treatment with HF, ignite at approximately 650°C . for about five minutes, cool, and weigh. The difference between the two weights is to be regarded as silica. Owing to the possible retention of some lead and zinc, the temperature of ignition should be rather closely controlled. This can be conveniently done in a muffle furnace.

By this method the authors obtained an average of 1.89 per cent of silica in the Bureau of Standards fluorspar No. 79. Eight of the cooperating analysts obtained an average of 1.87 per cent, the extreme results being 1.74 and 1.95 per cent. By the use of a method in which the fluorine was removed before the determination of silica, an average of 1.77 per cent was obtained by the authors.

5. CALCIUM FLUORIDE

(a) UMPIRE METHOD.—Transfer 0.5000 g of the sample (dried at 105 to 110°C .) to a 30 ml platinum crucible, add 15 ml of 10 per cent $\text{HC}_2\text{H}_3\text{O}_2$ and digest on the steam bath for one-half hour, stirring with a small glass rod at 5-minute intervals. Filter through a 7 cm filter paper of close texture and thoroughly wash the crucible and paper with small portions of hot water, using about 35 ml in all. Transfer the paper and precipitate to the crucible, dry, and ignite at a dull red heat.

Treat the residue in the crucible with about 3 ml of HF and evaporate to dryness. Add 1 to 2 ml of H_2SO_4 and evaporate to dryness under the hood. Cool, wash down the inside of the crucible with 1 ml more of H_2SO_4 (in order to catch any undecomposed particles of calcium fluoride), and again evaporate to dryness. Two or three evaporations with 3 to 4 ml of a 60 to 70 per cent solution of HClO_4 may be substituted for the evaporation with H_2SO_4 . Cool the

⁸ Add 20 ml of liquid bromine to 80 ml of glacial $\text{HC}_2\text{H}_3\text{O}_2$ and mix thoroughly. If liquid bromine comes in contact with the skin, painful burns will result which can be checked and relieved by quickly immersing and thoroughly rubbing the wound in carbon tetrachloride, and then allowing it to dry. The evaporation of the tetrachloride carries with it the free bromine.

⁹ A 20 per cent solution of KBr saturated with Br_2 . Transfer 500 g of Br to a liter bottle, add 700 ml of a 20 per cent solution of KBr, and cautiously shake. When the solution is exhausted, more of the 20 per cent solution of KBr may be added.

crucible and immerse it in a beaker containing 150 ml of dilute HCl (5:95). Warm gently and remove the platinum crucible, being sure to cleanse it from adhering particles of CaSO_4 .

Boil the contents of the beaker for 10 minutes, and if any insoluble matter remains, filter, wash, and ignite the residue in platinum.¹⁰

Pass H_2S into the clear filtrate for a few minutes and then make the solution ammoniacal. Continue the current of gas for 10 minutes and allow the precipitate to settle for 20 to 30 minutes. Filter and wash with $\text{NH}_4\text{Cl} - (\text{NH}_4)_2\text{S}$ solution.¹¹

Neutralize the filtrate and washings with HCl, add 20 ml of the acid in excess, and boil for two to three minutes to expel most of the H_2S . Add $\text{KBr} - \text{Br}_2$ solution¹² until the solution remains yellow, boil until the finely divided sulphur has been oxidized, and continue the boiling until the bromine has been expelled. Filter if sulphur or sulphides are not removed by the treatment with bromine. Precipitate the calcium in the filtrate in a volume of about 200 ml by adding 2 g of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and then NH_4OH slowly and with stirring until the solution is slightly ammoniacal. Heat on the steam bath for one-half to one hour, stirring occasionally, cool to room temperature, and filter on a paper of close texture. Wash with a cold 0.1 per cent solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, ignite to constant weight, and calculate the CaO to CaF_2 (factor = 1.392). The determination may be finished by titrating the calcium oxalate with a standard solution of KMnO_4 . In this case filter through a platinum or asbestos pad, finally wash the CaC_2O_4 with three or four 10 ml portions of cold water, and titrate as usual. To the CaF_2 found should be added 0.20 per cent to allow for the fluoride dissolved by the $\text{HC}_2\text{H}_3\text{O}_2$ and this result then corrected in accordance with the results obtained in a blank carried through all steps of the determination.

It is believed that analyses made by this method should be accurate to ± 0.25 per cent.

The use of platinum crucibles for the initial digestion with $\text{HC}_2\text{H}_3\text{O}_2$ obviates the quantitative transfer of the residue to the paper, and this saves time and keeps the volume of the washing solution at a minimum. Digestion can, however, be carried out in small glass beakers. A small rod just a little longer than the depth of the crucible is very convenient to use in stirring the solution during the digestion and to

¹⁰ This residue may consist of BaSO_4 , PbSO_4 , or undecomposed CaF_2 . Owing to the small size of the sample originally taken, it is not advisable to determine lead and barium at this point. The residue should be treated, however, with a few drops of HF and H_2SO_4 , heated until these are expelled, digested with 1 to 2 ml of HCl on the steam bath, and the solution added to the main solution for the determination of calcium. If the original material contains much barium, more or less BaSO_4 separates, but this is of no consequence.

¹¹ Prepared by passing a moderate stream of H_2S for five minutes through a solution containing 5 ml of NH_4OH and 10 g of NH_4Cl per liter.

¹² A 20 per cent solution of KBr saturated with Br_2 . See method for silica. The addition of $\text{KBr} - \text{Br}_2$ solution soon after acidification is more efficacious in removing sulphur than it would be if the boiling were continued until sulphur coagulated and the $\text{KBr} - \text{Br}_2$ then added.

pour against as the solution is transferred from the crucible to the paper.

After the treatment with $\text{HC}_2\text{H}_3\text{O}_2$, particles of the residue adhere to the surface of the crucible near the rim. These should be brushed to the bottom of the crucible with a piece of moist filter paper.

Sulphur is removed before calcium is precipitated, because sulphite or sulphate is formed when calcium oxalate containing sulphur is ignited, and in large precipitates these can not be entirely decomposed even by strong ignition. Results would consequently be high. Removal of sulphur is not needed if titration is to follow.

The results given under the umpire method in Table 1 are averages of closely agreeing analyses made by the authors. By the use of the method, 12 chemists who cooperated in the analysis of Bureau of Standards sample of fluorspar No. 79 obtained an average of 94.88 per cent of CaF_2 with variations from 94.72 to 95.27.

(b) ROUTINE METHOD.—Add 3 to 5 ml of 60 to 70 per cent HClO_4 to the residue obtained in the determination of silica as already described and evaporate to dryness in a radiator or over an asbestos gauze. Repeat the evaporation with HClO_4 , cool, add 3 to 5 ml of dilute HCl (5:95), warm slightly, and transfer the solution and any residue to a beaker. Add 3 to 5 ml of HClO_4 , again evaporate to dryness, cool, and take up the residue in 100 ml of dilute HCl (5:95). The solution at this point should be clear unless the original material contains much barium and sulphur. BaSO_4 , if present, does not interfere. Transfer the solution to a 250 ml graduated flask, make up to volume, mix well, and pipette a 100-ml portion into a 400-ml beaker. Heat the solution nearly to boiling, add NH_4OH until methyl red just turns yellow, and then a solution of $\text{H}_2\text{C}_2\text{O}_4$ (10 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ per 100 ml of water) dropwise until the red color reappears. Now add 10 ml of the $\text{H}_2\text{C}_2\text{O}_4$ solution and 50 ml of a saturated solution (about 4 per cent) of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. Digest on the steam bath for one-half to one hour, cool to room temperature, filter through a platinum or asbestos pad in a perforated crucible, wash the beaker and precipitate a few times with cold water.¹³ Return the crucible and precipitate to the beaker in which the precipitation was performed, add 100 ml of dilute H_2SO_4 (5:95), heat nearly to boiling, and titrate with 0.2 *N* KMnO_4 . Multiply the number of ml required by 2.5 and then by the titer of the solution. (1 ml of 0.2 *N* KMnO_4 = 0.00781 g of CaF_2 .) To the result should be added 0.0050 g of calcium fluoride to correct for that dissolved during the treatment with acetic acid and the solution of potassium bromide and bromine.

This method should be used for routine analyses only. The results should be accurate to ± 0.5 per cent, although in most cases

¹³ Filtration can be made through paper if desired. In this case, the washed precipitate should be sluiced into the beaker and the paper added just before the end point is obtained.

the accuracy is better than this, as is indicated in Table 1. By the routine method five of the cooperating analysts obtained an average of 94.8 per cent, with variations from 94.7 to 95.1.

TABLE 1.—Results for CaF_2 obtained by the use of the recommended methods

Material	CaF_2 indicated		
	Umpire method		Routine method
	Gravimetric, weighing as CaO	Volumetric, titration with KMnO_4	
1. B. S. fluorspar No. 79	Per cent 94.96	Per cent 94.91	Per cent 94.81
2. Bethlehem Steel Co.s standard "Q" (recommended value 85.25 per cent)	85.18	85.0	84.88
3. Pure CaF_2 to which was added CaCO_3 , PbS , ZnS to make 6 per cent of each	99.94	-----	99.57

6. SULPHUR

Mix 1.000 g of the sample in a platinum crucible with 10 g of K_2CO_3 and 0.5 g of KNO_3 , place the covered crucible in the muffle of an electric furnace, and heat until the mass is completely fused and the melt is quiet. An alcohol or petroleum ether flame may be used if an electric muffle is not available. When fusion is complete, gently rotate the crucible so that the cooling melt will solidify in a layer on the walls. Place the cooled melt in a beaker containing 150 ml of warm water, digest on the steam bath and stir occasionally.

When the melt is disintegrated, filter and wash the residue thoroughly with small portions of hot water. Acidify the filtrate with HCl and add 20 to 25 ml of HCl in excess. Evaporate to dryness, wash down the inside of the beaker, again add 20 to 25 ml of HCl , and evaporate to dryness. Dissolve the salts in 100 ml of dilute HCl (2:98), filter, wash with hot water, and add 5 ml of a 5 per cent solution of $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ to the filtrate, which should have a volume of approximately 150 ml. Boil for 10 to 15 minutes, allow to stand for four hours or preferably overnight, filter, wash with hot water, ignite, and weigh as BaSO_4 . A blank on the reagents should be carried through all steps of the method.

In analyses made by the authors an average value of 0.132 per cent as compared with the certificate value 0.14 was obtained for the Bureau of Standards standard fluorspar No. 79, and 0.28 per cent as compared with a recommended value of 0.27 per cent for a standard sample of fluorspar prepared by the chemists of the Bethlehem Steel Co.¹⁴

¹⁴ Sample furnished by W. E. Steiner, chief chemist of the Bethlehem Steel Co., Cambria plant, Johnstown, Pa.

7. BARIUM

Transfer 5.00 g of sample to a platinum dish and digest on the steam bath for 10 minutes with 10 ml of HF. Then add 5 ml of HNO_3 and 25 ml of 60 to 70 per cent HClO_4 and evaporate to dryness. Again add 25 ml of HClO_4 and evaporate to dryness. Repeat the addition of HClO_4 and again evaporate. Take up the dry mass in 50 ml of dilute HCl (1:9) and heat to boiling. If a residue remains, filter, wash with warm water, ignite at as low a temperature as possible, and treat with 5 to 10 ml of HF and 5 to 10 drops of H_2SO_4 . Expel the acids at a low temperature, fuse with about 1 g of Na_2CO_3 , and extract the melt with water. Filter, wash the paper and residue with hot water, dissolve the residue in HCl , avoiding more than a few drops in excess, and add the clear solution to the main one. Dilute the combined solutions to 200 ml, heat nearly to boiling, and add dropwise and with stirring 4 ml of dilute H_2SO_4 (1:3). Boil for 15 minutes and digest on the steam bath for three to four hours. Do not allow the solution to cool below 40° to 50° C., because of the tendency of CaSO_4 to separate. If a precipitate forms, filter, wash with hot dilute HCl (1:99), and then with cold water. Ignite the precipitate and weigh as BaSO_4 .

If lead is present in appreciable amount, the BaSO_4 may be contaminated by PbSO_4 . To correct for this, add 5 ml of a 20 per cent solution of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ to the weighed precipitate, digest on the steam bath for 30 minutes, filter, and wash with hot water. Add a few drops of HCl to the filtrate, treat with H_2S , and if any PbS forms, remove it by filtration, cautiously ignite it at a dull red heat, treat with a few drops of HNO_3 and H_2SO_4 , and again ignite at a dull red heat. Subtract the weight of PbSO_4 here found from that of the mixed sulphates and calculate the percentage of BaO or BaSO_4 . A corresponding correction should also be made in the subsequent determination of lead.

8. LEAD

Pass H_2S for a few minutes into the filtrate obtained in the barium determination and then render the solution slightly ammoniacal. Continue the current of H_2S for 10 minutes and allow the solution to stand at the side of the steam bath for 30 minutes. Filter, wash a few times with NH_4Cl -(NH_4) $_2\text{S}$ solution, and discard the filtrate. Dissolve the precipitate in 25 ml of hot dilute HNO_3 (1:2), dilute the solution, and repeat the precipitation and washing in order to eliminate all calcium which might otherwise be precipitated with the lead. Dissolve the precipitate in HNO_3 as before, add 3 ml of H_2SO_4 , and evaporate until dense fumes of the acid appear. Cool, dilute with water to 50 ml, and allow to stand for three hours or over night. Filter, wash a few times with cold dilute H_2SO_4 (1:20), ignite the precipitate very cautiously to dull redness (preferably in

a muffle or radiator), and weigh as PbSO_4 . If the sulphate was caught on paper instead of asbestos, the ignited residue should be treated with HNO_3 and H_2SO_4 before the final ignition.

The filtrate from the PbSO_4 may contain a trace of lead. To recover this and to free the solution from platinum before zinc is determined, adjust the acidity by neutralizing with NH_4OH and then adding 2 ml of H_2SO_4 per 100 ml of solution. Treat with H_2S , and if a precipitate forms, filter, wash, and cautiously ignite the residue at a low temperature. Treat with a few drops of H_2SO_4 and HNO_3 , again ignite at a very dull red heat, and weigh. Add 5 ml of a 20 per cent solution of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, allow to stand on the steam bath for 30 minutes, filter, ignite in the same crucible, and again weigh. The difference between the two weights represents PbSO_4 which should be added to that already obtained. This correction is usually so small that it need not be made except in very accurate work. The treatment with H_2S in acid solution, however, should be made to remove the trace of lead and the varying amounts of platinum which may be present. Otherwise these would subsequently contaminate the zinc.

9. ZINC

After having removed lead and platinum, boil the filtrate to remove H_2S , add methyl orange, carefully neutralize the solution, and then add enough H_2SO_4 to make the solution 0.01 *N*. If iron or aluminum are present in large amounts, they must be removed before the acidity is adjusted, for otherwise they will be precipitated in part. Pass a stream of H_2S through the cool solution for 30 minutes, allow to stand for one hour, filter on a paper of close texture, and wash with cold water. Ignite at a low temperature until the carbon of the paper is gone and then at a dull red. Weigh as ZnO .

10. OTHER CONSTITUENTS

The oxides of iron and aluminum may be determined by the usual procedures after fluorine has been volatilized by fuming with H_2SO_4 or HClO_4 . Alkalies may be determined by the J. Lawrence Smith method.

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